

**State-resolved rotational cross sections and thermal rate
coefficients for *ortho*-/*para*-H₂+HD at low temperatures and
HD+HD elastic scattering**

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Abstract

Results for quantum mechanical calculations of the integral cross sections and corresponding thermal rate coefficients for para-/ortho-H₂+HD collisions are presented. Because of significant astrophysical interest in regard to the cooling of primordial gas the low temperature limit of para-/ortho-H₂+HD is investigated. Sharp resonances in the rotational state-resolved cross sections have been calculated at low energies. These resonances are important and significantly contribute to the corresponding rotational state-resolved thermal rate coefficients, particularly at low temperatures, that is less than $T \sim 100\text{K}$. Additionally in this work, the cross sections for the elastic HD+HD collision have also been calculated. We obtained quite satisfactory agreement with the results of other theoretical works and experiments.

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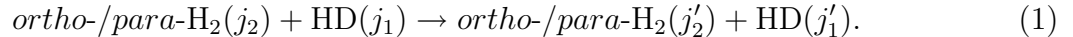
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I. INTRODUCTION

We report rotational state-resolved cross sections and corresponding thermal rate coefficients for the fundamental elastic and inelastic collisions between hydrogen molecules in both *ortho*- and *para*- states and its isotopic partner, the HD molecule:



Here H is hydrogen and D is deuterium. HD is the second most abundant primordial molecule after H_2 and plays an important role in the chemistry of the interstellar medium [1], more specifically in rotational energy transfer collisions (1) [2, 3, 4]. Also, HD itself is of interest as a light molecule with a small but constant dipole moment $|\vec{d}| = (8.1 \pm 0.5) \cdot 10^{-4}$ D [5]. This ability of HD makes the study of this molecule an important undertaking in astrophysics and other fields, such as in condensed matter physics, see for instance [6].

Furthermore, H_2 and HD molecules play a significant role in the formation of the primary stars in the Universe [7, 8], where the dynamics of $\text{H}_2 + \text{H}_2$, $\text{H}_2 + \text{HD}$ and $\text{HD} + \text{HD}$ molecular collisions can make a substantial contribution to the formation of the primordial structure of stars [9]. The spectroscopic measurements from distant quasars with H_2 and HD molecules in the cold gases around them or on the line of sight can be very important and requires detailed knowledge of the cross sections at low energies [10, 11].

Although the field of molecular collisions between hydrogen molecules and its different isotopic combinations: $\text{H}_2 + \text{D}_2$, $\text{D}_2 + \text{HD}$, $\text{HD} + \text{HD}$ and others, have already a rather long research history [12, 13, 14, 15, 16, 17, 18], there are substantial discrepancies between the results of different research groups. The recent appearance of the new potential energy surface for the H_4 system makes it very useful to carry out new calculations for these important systems.

By now the deuterium chemistry of the early Universe has been extensively studied by a few research groups, see for example, [2] and [3, 4]. In these works the authors carried out quantum-mechanical state-resolved calculations for a wide range of temperatures. Schaefer's work [2] presents results for the thermal rate coefficients at very low temperatures down to ~ 10 K. The corresponding cross sections have been calculated at collisional velocities ~ 12 m/s, which are almost equal to ultra-low energies.

The author of work [3] used Schwenke's modified $\text{H}_2\text{-H}_2$ potential [19, 20]. Schaefer applied a different surface, which was also a modification of older PESs, see for example

[21]. However, as we already mentioned, the importance of the H_2+HD rotational energy transfer collisions makes it very reasonable to carry out new calculations for the systems with the use of the BMKP PES published in 2002 which provides the latest and presumably most accurate H_4 surface [22].

In this work the scattering cross sections and their corresponding thermal rate coefficients are calculated using a non reactive quantum-mechanical close-coupling approach. In the work [4] we already presented the details of the method we used, therefore in this work we continue beyond that point with the results for *ortho*- H_2+HD . The calculations are done for very low and low temperatures from 5 K to up to 300 K. Atomic units ($e = m_e = \hbar = 1$) are used throughout these calculations.

II. RESULTS

Before undertaking production calculations we carried out a large number of test calculations to insure the convergence of the results with respect to all parameters that enter into the propagation of the Schrödinger equation [23]. The details of the quantum-mechanical computation approach are presented in [24]. The same test calculations were carried out in our previous works [25, 26] for the *ortho*-/*para*- H_2+H_2 collisions, which involved the intermolecular distance R_3 , the total angular momentum J of the four atomic system, the number of rotational levels to be included in the close coupling expansion $N_{l_{\text{tot}}}$ and others.

In these calculations the *VRTP* mechanism has been used, which allows us to specify $V(\vec{R}_1, \vec{R}_2, \vec{R}_3)$ explicitly rather than to expand the potential in angular functions, see the MOLSCAT manual [23]. As in our previous works we reached convergence for the integral cross sections, $\sigma(j'_1, j'_2; j_1 j_2, \epsilon)$, in all considered collisions. However, we have found in this work, that in the case of *ortho*- H_2+HD the convergence is slower than in the case of *para*- H_2+HD .

A. *ortho*-/*para*- H_2+HD and $\text{HD}+\text{HD}$ cross sections

In Fig. 1 we present the results for the low energy *ortho*-/*para*- $\text{H}_2 + \text{HD}$ and $\text{HD}+\text{HD}$ elastic scattering collisions. In these calculations the collision energy ranges from 10^{-5} cm^{-1} to 100 cm^{-1} . As can be seen at energies less than $\sim 5 \cdot 10^{-4} \text{ cm}^{-1}$ the elastic cross sections,

σ_{el} , display almost constant values. This result is in good agreement with the non-relativistic quantum-mechanical scattering theory, that is at very low collision energies:

$$\sigma_{el}(E_{coll} \sim 0) = \pi a_0^2 = \text{const}, \quad (2)$$

where a_0 is the scattering length [27]. From our calculations in the case of *ortho*-H₂+HD: $\sigma_{el} = \pi a_0^2 = 380.70 \cdot 10^{-16} \text{ cm}^2$. The corresponding scattering length is $a_0(\textit{ortho}\text{-H}_2 + \textit{HD}) = 11.01 \cdot 10^{-8} \text{ cm}$. A rather sharp resonance is found in this cross section at energies around 0.56 cm^{-1} . The value of this resonance is $\sigma_{res}(\textit{ortho}\text{-H}_2 + \textit{HD}) = 1,897.8 \cdot 10^{-16} \text{ cm}^2$.

Below, in the same figure we also present the results from a *para*-H₂+HD scattering cross section. These results were not shown in [4]. Further, we computed the HD+HD elastic collision. These calculations are also done with the BMKP PES. Fig. 1 shows this result. It is seen, that the behaviour of all three cross sections is almost identical, although the values are rather different. Again, the collision energy ranges from 10^{-5} cm^{-1} to 100 cm^{-1} . At energies less than $\sim 5 \cdot 10^{-4} \text{ cm}^{-1}$ the elastic cross sections display almost constant values: $\sigma_{el}(\textit{para}\text{-H}_2 + \textit{HD}) = 380.031 \cdot 10^{-16} \text{ cm}^2$, and $\sigma_{el}(\text{HD} + \text{HD}) = 274.84 \cdot 10^{-16} \text{ cm}^2$. The corresponding scattering lengths are: $a_0(\textit{para}\text{-H}_2 + \textit{HD}) = 11.0 \cdot 10^{-8} \text{ cm}$ and $a_0(\text{HD} + \text{HD}) = 9.35 \cdot 10^{-8} \text{ cm}$.

Sharp resonances have been calculated at energies around 0.57 cm^{-1} in the case of *para*-H₂+HD and around 2.05 cm^{-1} for HD+HD. The values of these resonances are the following: $\sigma_{res}(\textit{para}\text{-H}_2 + \textit{HD}) = 1,888.84 \cdot 10^{-16} \text{ cm}^2$ and $\sigma_{res}(\text{HD} + \text{HD}) = 737.43 \cdot 10^{-16} \text{ cm}^2$.

Next, one can see from Fig. 1, that the elastic cross sections are closely related to each other and the calculated values of a_0 's have reasonably similar values. However there are significant differences in the positions and the values of the resonances between *ortho*-/*para*-H₂+HD and HD+HD collisions. The reason for these differences is due to the permanent dipole moment of the HD molecules. This phenomenon is important at low energies and is responsible for the energy shift in the total Hamiltonian of the four-atomic systems. The additional interaction makes the shift of the position of the high value resonance in HD+HD elastic cross section relative to the positions of the resonances in the *ortho*-/*para*-H₂+HD systems.

In addition to the results of Fig. 1 in Fig. 2 our HD+HD elastic cross sections are shown together with the corresponding results from paper [13]. Please see Fig. 16 and Fig. 17 of [13], where theoretical and some experimental results for HD+HD are presented. It is seen,

that the trend of the both cross sections is similar to each other, this is important, although the values are rather different at some collisional energies (velocities). We consider these results as a quite sufficient test of our calculations for the HD+HD collisions.

Fig. 3 shows results for the state-resolved cross sections $\sigma(j'_1 j'_2; j_1 j_2)(\epsilon)$ in the *ortho*-case of the collision (1). In the upper and middle plots we present our data for the $(j_1 = 1, j_2 = 1) \rightarrow (j'_1 = 0, j'_2 = 1)$ and $(j_1 = 2, j_2 = 1) \rightarrow (j'_1 = j'_2 = 1)$ quantum transitions together with the results of Schaefer's work [2], which applied a modified version of Schwenke's potential [20] and a different dynamical quantum-mechanical method. In the lower plot results for $(j_1 = 2, j_2 = 1) \rightarrow (j'_1 = 0, j'_2 = 1)$ are presented together with the results of work [2]. The values of this channel cross section are lower by factor of 10 than in the case of the two previous cross sections.

As can be seen for the transition quantum states $(j_1 = 1, j_2 = 1) \rightarrow (j'_1 = 0, j'_2 = 1)$ and $(j_1 = 2, j_2 = 1) \rightarrow (j'_1 = j'_2 = 1)$ the agreement between our results and Schaefer's calculations is fairly good. However, for the $(j_1 = 2, j_2 = 1) \rightarrow (j'_1 = 0, j'_2 = 1)$ channel cross section we found significant disagreements in the cross section. The difference between our cross section and Schaefer's results reaches the factor of 2 at a collisional velocity around 270 m/s.

In conclusion, in the case of *ortho*-/*para*-H₂+HD we reproduced all sharp resonances in the low energy region [4]. These high value cross sections should contribute significantly to the cooling process of the astrophysical media, therefore it is of crucial importance to carry out calculations for these cross sections accurately. However, in the case of higher transition states we found some disagreements (up to 100%) in the cross sections with work [2]. But these cross sections have values of relatively low magnitude.

B. *ortho*-/*para*-H₂+HD thermal rate coefficients

In this section we present new results for thermal rate coefficients regarding the case of *ortho*-/*para*-H₂+HD. Corresponding cross sections have been presented in the previous section and some of them have been published in work [4]. In [4] we were able to reproduce all relevant resonances in the cross sections for different rotational channels [2], however significant differences and new resonances have been found in the cross sections with higher values of the rotational transition states.

Fig. 4 shows temperature dependent thermal rate coefficients corresponding to two relevant cross sections from Fig. 2: for $(j_1 = 1, j_2 = 1) \rightarrow (j'_1 = 0, j'_2 = 1)$ and $(j_1 = 2, j_2 = 1) \rightarrow (j'_1 = j'_2 = 1)$ quantum-mechanical rotational transition states. Again agreement with work [2] is very good. However there is significant disagreement with results of work [3].

Fig. 5 presents our results together with Schaefer's data from [2] for the $(j_1 = 1, j_2 = 0) \rightarrow (j'_1 = j'_2 = 0)$, $(j_1 = 2, j_2 = 0) \rightarrow (j'_1 = 1, j'_2 = 0)$ and $(j_1 = 2, j_2 = 0) \rightarrow (j'_1 = j'_2 = 0)$ thermal rate coefficients. One can see, that the first two thermal rates agree very well with the results of work [2], however the third (lower plot) is not in good agreement. As in Fig. 3, there is significant disagreement with the corresponding results of work [3].

In [4] and in this work we provide cross sections and corresponding thermal rates for only relevant transition states, that is transitions with relatively high cross sections. Detailed calculations for many other transition quantum numbers and, probably, for collisions of other hydrogen isotopes should be done in the future.

Through this analysis we can conclude, that the BMKP PES can reproduce the general behaviour of all considered cross sections and thermal rates in the *ortho/para*-H₂+HD collisions. For the lower quantum states we obtained sufficient agreement with the results of work [2] and significant disagreement with [3]. Also, for transition states with higher values the BMKP PES provides rather small cross sections and thermal rate coefficients relative to the corresponding results of work [2].

III. CONCLUSION

In this work the state-resolved close-coupling quantum-mechanical calculations for rotational excitation and de-excitation cross sections of the *ortho/para*-H₂+HD and HD+HD collisions are presented. The latest, global BMKP surface for the H₂-H₂ system has been appropriately adopted for H₂+HD and HD+HD. The linear rigid rotor model for the H₂ and HD molecules is applied. A test of convergence and the results for cross sections with the BMKP PES are obtained for a wide range of kinetic velocities including very low values down to ~ 10 m/s. As in work [4] these results revealed, that the applied quantum-mechanical method together with the BMKP PES is able to provide reliable cross sections and thermal rate coefficients in collisions (1).

An interesting result of this work lies in the comparison between our calculations with the BMKP PES, calculations of [3], and with the results of [2]. As we mentioned, these works used pure quantum mechanical methods, but within the rigid rotor approximation: the distances between hydrogen atoms in the H₂ or HD molecules have been fixed. These works used different H₄ potential energy surfaces. In Fig. 3 we showed that our results for the state-resolved cross sections $\sigma_{nl \rightarrow n'l'}(E_{coll})$ are close to the corresponding cross sections of the relatively old work [2]. Furthermore, because the state-resolved thermal rate coefficients $k_{nl \rightarrow n'l'}(T)$ are less sensitive to different collision parameters, for instance, interaction potentials, for $k_{nl \rightarrow n'l'}(T)$ we obtained even better agreement with the results of work [2]. This is seen in Figs. 4 and 5.

However, the same type comparisons with the corresponding thermal rate coefficients from the newer work [3] demonstrated substantial disagreements, which are also seen in Figs. 4 and 5. The deflection between results of [3] and our data and Schaefer's results can reach almost 60%. In future works it will be very useful for comparison purposes to adopt other precise H₄ PES from the work [28] and apply it to the ortho-/para-H₂+HD collisions. The Deep and Johnson potential energy surface (DJ PES) was already successfully applied to H₂+H₂ in [25, 26, 29]. Also, it seems to us that it would be very useful to carry out new calculations for various differential cross sections $d\sigma_{nl \rightarrow n'l'}(\theta, \varphi)/d\Omega$ for the H₂+H₂/HD collisions as in [30] with the use of different PESs.

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- Fig. 1** Elastic scattering cross section for *ortho*-H₂+HD, *para*-H₂+HD and HD+HD at ultralow collision energies. Calculations are done with the BMKP PES.
- Fig. 2** Elastic scattering cross section for HD+HD calculated with the use of the BMKP PES and the corresponding result from work [13].
- Fig. 3** Rotational state resolved integral cross sections for *ortho*-H₂(j_2) + HD(j_1) → H₂(j'_2)+HD(j'_1). Upper plot: initial states of HD and H₂ molecules are $j_1 = j_2 = 1$ and corresponding final states are $j'_1 = 0$ and $j'_2 = 1$. In the bottom plots: $j_1 = 2$, $j_2 = 1$ and the corresponding final states are $j'_1 = j'_2 = 1$ and $j'_1 = 0$, $j'_2 = 1$. Calculations are done with the BMKP PES (bold lines), circles, diamonds and triangles up are corresponding results from work [2].
- Fig. 4** Rotational state resolved thermal rate coefficients for *ortho*-H₂(j_2) + HD(j_1) → H₂(j'_2) + HD(j'_1). In the upper plot the initial states of HD and H₂ molecules are $j_1 = j_2 = 1$ and the corresponding final states are $j'_1 = 0, j'_2 = 1$. In the bottom plot, $j_1 = 2, j_2 = 1$ and corresponding final states are $j'_1 = j'_2 = 1$. Calculations are done with the BMKP PES (bold lines), triangles up and squares are corresponding results from work [2]. Results from work [3] are also shown.
- Fig. 5** Rotational state resolved thermal rate coefficients for *para*-H₂(j_2) + HD(j_1) → H₂(j'_2) + HD(j'_1). Upper plot: initial states of HD and H₂ molecules are $j_1 = 1$ and $j_2 = 0$ and corresponding final states are $j'_1 = j'_2 = 0$. In the bottom plots: $j_1 = 2, j_2 = 0$ and the corresponding final states are $j'_1 = 1, j'_2 = 0$ and $j'_1 = j'_2 = 0$. Calculations are done with the BMKP PES (bold lines), circles, triangles up and diamonds are corresponding results from work [2]. Results from work [3] are also shown.

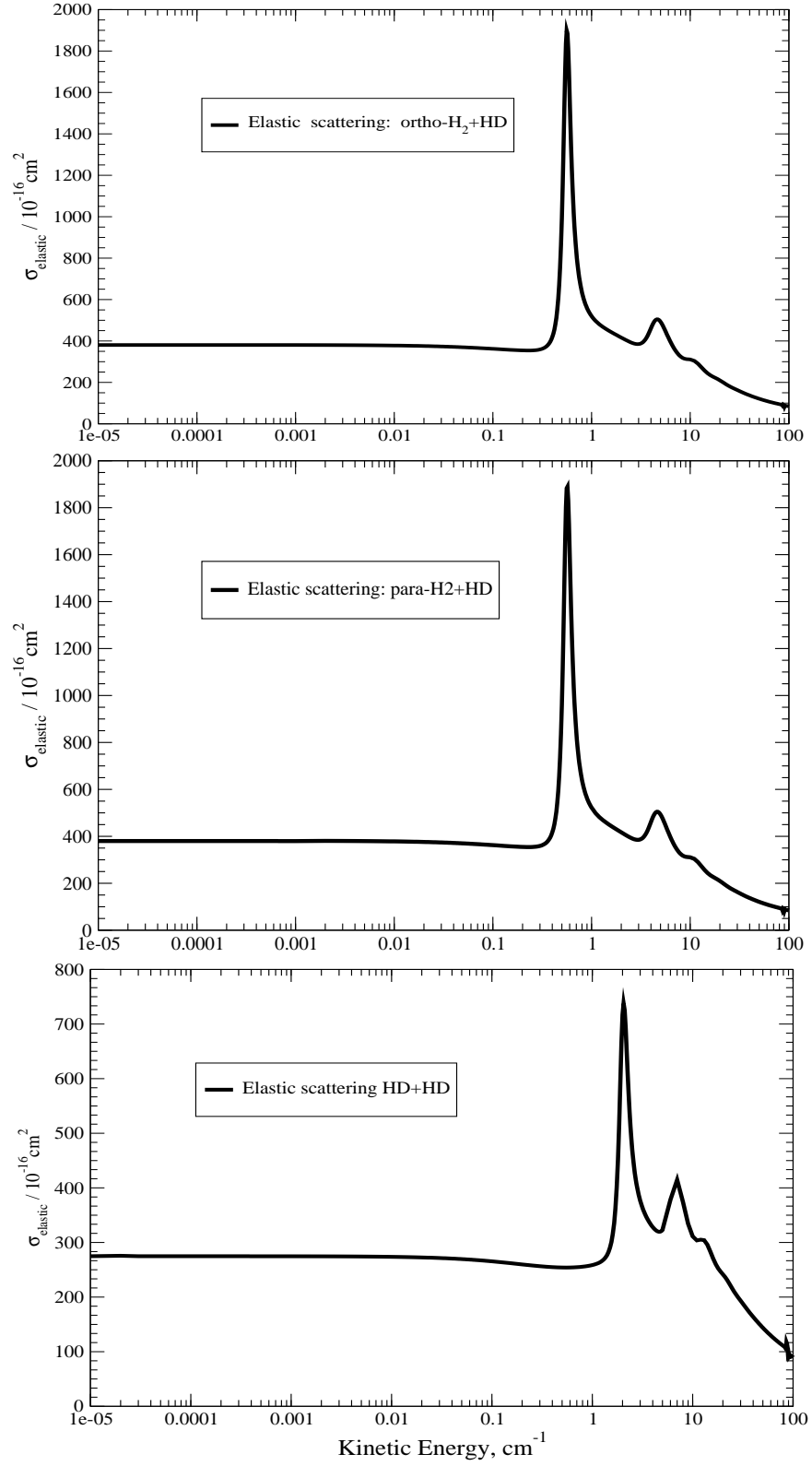


FIG. 1: Elastic scattering cross section for *ortho*-/*para*-H₂+HD and HD+HD at ultralow collision energies. Calculations are done with the BMKP PES.

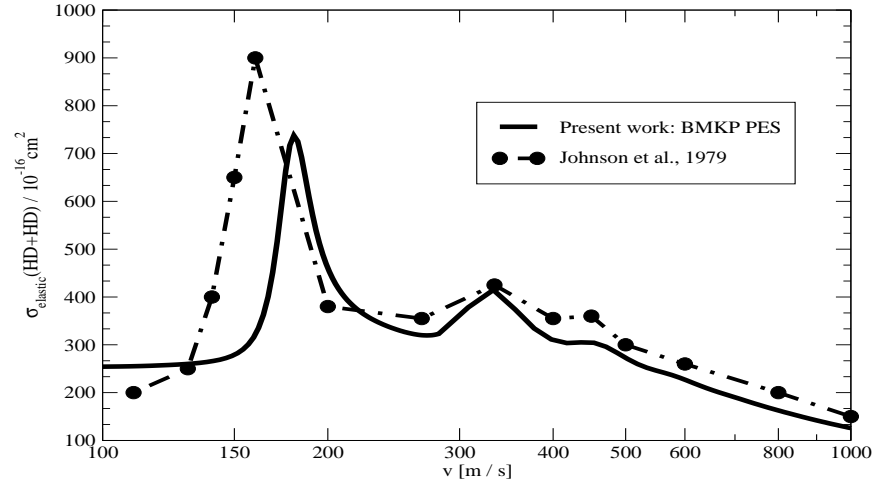


FIG. 2: Elastic scattering cross section for HD+HD calculated with the use of the BMKP PES and the corresponding result from work [13].

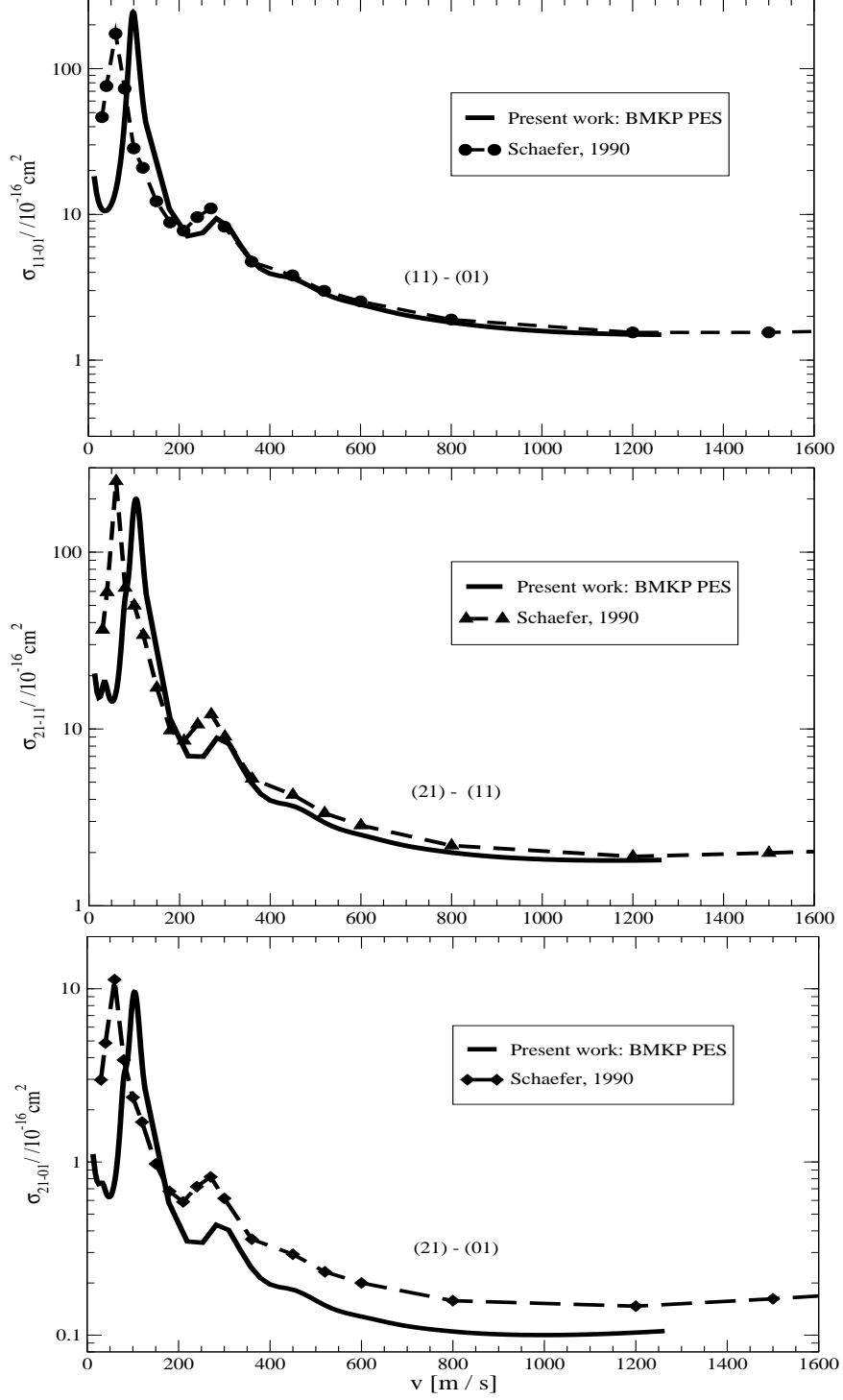


FIG. 3: Rotational state resolved integral cross sections for *ortho*-H₂(*j*₂) + HD(*j*₁) → H₂(*j*₂') + HD(*j*₁'). Upper plot: initial states of HD and H₂ molecules are *j*₁ = *j*₂ = 1 and corresponding final states are *j*₁' = 0 and *j*₂' = 1. In the bottom plots: *j*₁ = 2, *j*₂ = 1 and the corresponding final states are *j*₁' = *j*₂' = 1 and *j*₁' = 0, *j*₂' = 1. Calculations are done with the BMKP PES (bold lines), circles, diamonds and triangles up are corresponding results from work [2].

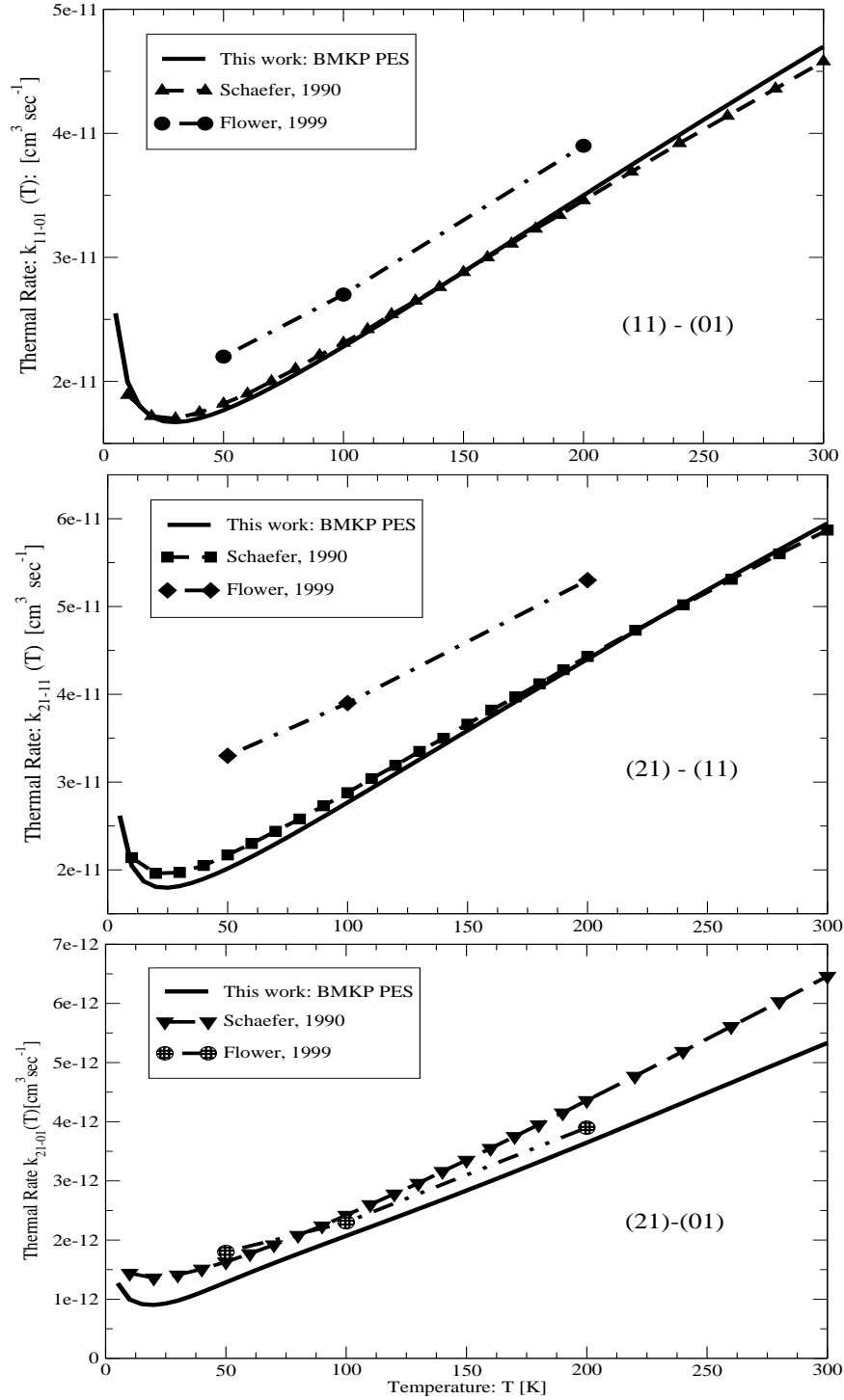


FIG. 4: Rotational state resolved thermal rate coefficients for $ortho\text{-H}_2(j_2) + \text{HD}(j_1) \rightarrow \text{H}_2(j'_2) + \text{HD}(j'_1)$. In the upper plot the initial states of HD and H_2 molecules are $j_1 = j_2 = 1$ and the corresponding final states are $j'_1 = 0, j'_2 = 1$. In the bottom plot, $j_1 = 2, j_2 = 1$ and corresponding final states are $j'_1 = j'_2 = 1$. Calculations are done with the BMKP PES (bold lines), triangles up and squares are corresponding results from work [2]. Results from work [3] are also shown.

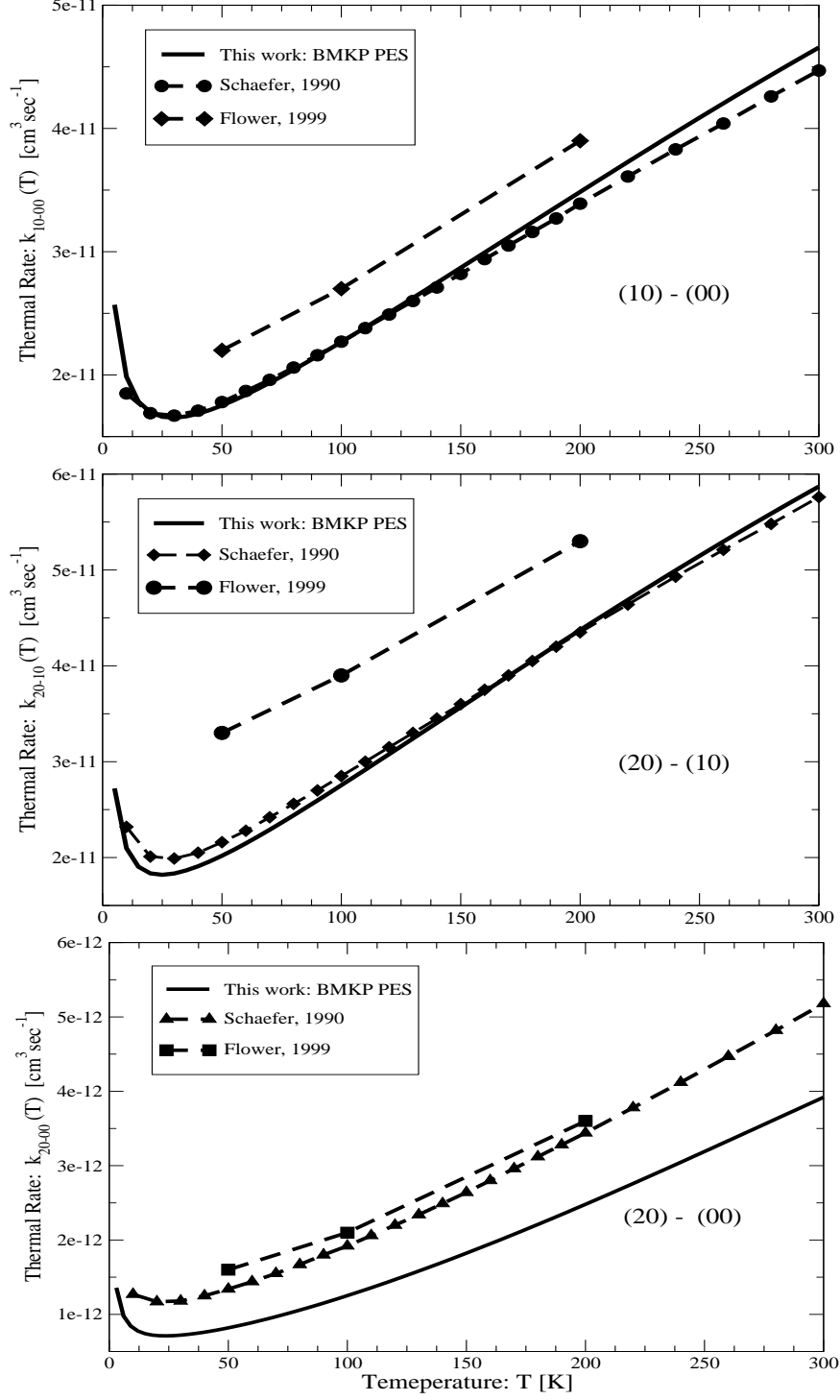


FIG. 5: Rotational state resolved thermal rate coefficients for $\text{para-H}_2(j_2) + \text{HD}(j_1) \rightarrow \text{H}_2(j'_2) + \text{HD}(j'_1)$. Upper plot: initial states of HD and H_2 molecules are $j_1 = 1$ and $j_2 = 0$ and corresponding final states are $j'_1 = j'_2 = 0$. In the bottom plots: $j_1 = 2$, $j_2 = 0$ and the corresponding final states are $j'_1 = 1$, $j'_2 = 0$ and $j'_1 = j'_2 = 0$. Calculations are done with the BMKP PES (bold lines), circles, triangles up and diamonds are corresponding results from work [2]. Results from work [3] are also